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WVT-6605

PROCESS FOR ANODIZING TITANIUM

TECHNICAL REPORT

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BY

THEODORE M. POCHILY

APRIL 1966

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U.S. ARMY WEAPONS COMMAND

WATERVLIET ARSENAL

WATERVLIET—NEW YORK

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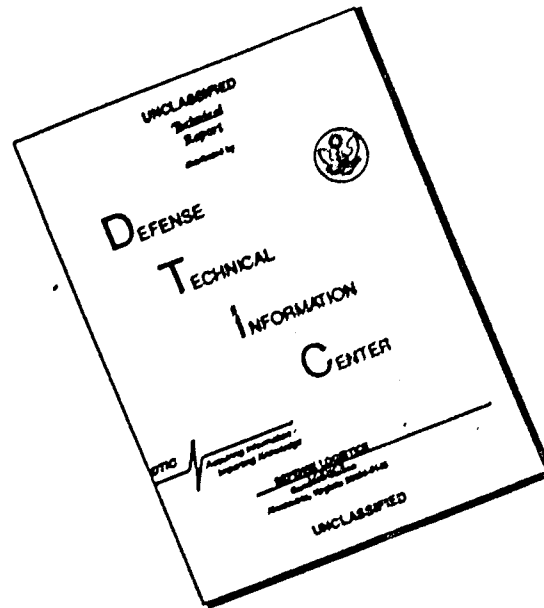
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Report No. WVT-6605, April 1966, 43 pages, 6 tables and 8 figures. AMCMS Code No. 4930.15.6267.20.01, DA Project No. 66267. Unclassified Report	
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(OVER)	
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Anodic Coatings	Anodic Coatings
Metal Finishing	Metal Finishing
Anodizing	Anodizing
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PROCESS FOR ANODIZING TITANIUM

ABSTRACT

The requirements of an advancing technology in weaponry, aircraft, and aerospace have necessitated a consideration of light metals as a substitute for steel. In the search to reduce weight, and consequently increase mobility, titanium offers valuable assistance. The use of titanium as an engineering and structural material has been accepted for a comparatively short time. This acceptance was predicated on two important factors, strength/weight ratio and corrosion resistance. The tendency of titanium to gall and seize, when used as a bearing or mating surface, has restricted a full utilization of the metal. Work conducted at Watervliet Arsenal to develop a process that reduces or eliminates this condition has been evaluated. Processing details, a summary of test data covering wear resistance, and the effects of the process on the mechanical properties of titanium are discussed.

Cross-Reference Data

Titanium
Anodic Coatings
Metal Finishing
Anodizing

TABLE OF CONTENTS

	Page
Abstract	1
Glossary	4
Objective	5
Introduction	5
Background	6
General	6
Electroless Nickel	6
Conversion Coatings	7
Approach to the Problem	8
Preparation for Processing	8
Materials and Equipment	9
Procedure	10
Results	13
Discussion of Results	19
Acid Electrolytes	19
Alkaline Electrolytes	19
Conclusions	21
Literature Cited	37
Selected Bibliography	39
Distribution List	41
DD Form 1473 (Document Control Data)	

Tables

I. Tensile Test	13
Ia. Tensile Test	14
Ib. Tensile Test - Ambient Temperature	15
II. Fatigue Test - Rotating Beam	16
III. Wear Test	17
IV. Application to Weapons Components	18

TABLE OF CONTENTS (Continued)

	Page
Figures	
1. Anodizing Racks	22
2. Electrolytic Solutions Utilized	23
2A. Electrolytic Solutions Utilized	27
2B. Electrolytic Solutions Utilized	29
2C. Electrolytic Solutions Utilized	30
3. Converted Anodized Film at 250X	32
4. Converted Anodized Film at 500X	32
5. Erosion Comparison Coated versus Uncoated Titanium Nozzles	33
6. Titanium Coated Components	34
7. Titanium Anodize Flow Sheet	35
8. Suggested Layout	36

GLOSSARY

a.s.i.	-	amps per square inch
a.s.f.	-	amps per square foot
A°	-	Angstrom
CD	-	current density
CP	-	chemically pure
Fe	-	iron
gm.	-	gram
HF	-	hydrofluoric acid
HNO ₃	-	nitric acid
hp.	-	horsepower
Kw.	-	kilowatt
ml.	-	milliliter
mm.	-	millimeter
Pb	-	lead
P.s.i.	-	pounds per square inch
Pt	-	platinum
R.P.M.	-	revolutions per minute
SS	-	stainless steel
V	-	Volts

OBJECTIVE

The objective of the program was to develop a coating process that would provide titanium with a hard, wear-resistant, antigalling surface. In addition, it was stipulated that the system should be comparatively simple and readily adaptable for production. It was further desired that a coating without any or at least a negligible effect on the physical and mechanical properties of the base metal be obtained.

INTRODUCTION

The requirements of modern weaponry and design have necessitated consideration of the lightweight metals as a substitute for steel. In the search to reduce weight, and consequently increase mobility, titanium offers valuable assistance. The use of titanium as an engineering or structural material has been accepted for a comparatively short time. These acceptances were predicated on two important factors, strength/weight ratio and corrosion resistances. Although considerable application of titanium has been found in the aircraft industries and aerospace design, a fuller utilization has been restricted due to its inherent tendency to gall and seize when used as a bearing surface. This condition has persisted despite extensive efforts to employ conventional and sophisticated lubricating systems. This galling tendency is evident in all metals, but in most cases, a means such as electroplating, nitriding, carburizing, or normal lubrication has been used to reduce or to eliminate this condition. Titanium, unlike most metals, has a tenacious oxide coating that reoccurs almost spontaneously. Consequently, the metal is not receptive to metal deposition except under sophisticated cleaning and deoxidizing procedures. This oxide interference presents a barrier to an intimate bond regardless of the type and manner of coating applied. The titanium fabricators have initiated countless investigations to overcome this unfavorable characteristic of titanium. Programs have ranged from vapor state deposition to simple conversion coatings. But to date, no simplified system has been found to produce a consistently adherent protective surface that will protect the metal under stress and strain. Many areas including the conventional type deposition systems and the complicated and expensive cladding, solution hardening, diffusion layers, nitriding, and carburizing processes, have been investigated. Although in some systems a hard surface layer is produced, the application of the processes is restricted due to severe embrittlement of the base metal and the coating. Further restrictions are imposed upon system acceptance due to the excessive heats required to develop or bond these coatings. Then too, high heats and exposure to oxygen, hydrogen, and ammonia during the coating process will drastically effect mechanical properties of the titanium.

The program was initiated specifically to provide a barrier layer that would reduce or eliminate the severe galling that occurs when titanium is subjected to rubbing or sliding forces. The magnitude or direction of force does not reflect the degree of galling. In the case of most other metals, some means of lubrication or protection have been

given to both or one member of the junction. Because titanium tends to flow when pressure is encountered, this preventative measure has been rather successful. Irrespective of the nature of lubrication, the tenacious oxide coating discourages intimate contact of the lubricant and the metal. Failure occurs when the barrier layer allows metal-to-metal contact. The time element involved is short and unfortunately is not a function of bearing load. Considerable investigation in recent years has been directed toward a solution to the problem. There have been several claims of success relevant to electro-deposited and anodized coatings. Despite these particular claims, it is rather obvious that the use of titanium has not appreciably increased its use in engineering. This factor is quite evident in the field of weaponry. Here, the use of titanium which was once regarded as the logical substitute for steels has not satisfied the exacting requirements of the designer. With the ever-increasing demands for greater fire power and mobility, the cannon and mortar designer cannot accept the possibility of a malfunction or seizure due to the inability of mating parts to function.

BACKGROUND

(A) General

The use of anodic oxidation has been a generally accepted procedure in the field of metal finishing for some time. Its application to metals such as aluminum and magnesium as a means of improving wear resistances and corrosion protection has clearly demonstrated the practicability of oxide coatings for these purposes. However, titanium unlike the preceding metals has had limited usefulness because of the absence of an acceptable coating. Restrictive properties, the tendency to gall and seize, when used as a bearing surface, regulated the role of titanium as an engineering and structural metal. Conversely, the excellent corrosion resistances, the favorable strength to weight ratio, and the excellent high temperature properties satisfy the requirements of an advancing design technology. The obvious obstacle in the acceptance of titanium was the problem of wear protection and lubrication. This obstruction stimulated an investigation which resulted in the development of an anodic coating capable of providing wear protection and of accepting a lubricant, if required.

(B) Electroless Nickel

Specific conditions existed at Watervliet Arsenal that reflected the problems noted above. The redesign of a mortar to reduce its overall weight utilized titanium as a replacement for steel. The design engineers selected the most acceptable approach available. Work, which utilized the electroless nickel deposition system with post thermal treatment, performed by private industry and later by the Watertown Arsenal, indicated a possible resolution of their problems. Unfortunately, the high temperature (1550°E) required for vacuum diffusion, proved to be prohibitive and several components distorted under this exposure. A means to improve the adhesion without a diffusion treatment was investigated at Watervliet. Various pretreatments and activating solutions 2,3,4,5,6 did not improve

the nickel in the as-plated condition. With basically the same problem in evidence, a continually reoccurring oxide film, additional work followed with the use of intermediate coatings such as copper⁷, silver⁸, iron⁹, and zinc⁷. As the investigation progressed, it became more apparent that the presence of water or the exposure to air did nullify any cleaning procedure. In addition, it must be concluded a strong possibility exists that some reported successes were the result of total or near total mechanical bonding.

Nonaqueous solutions⁷ were thought to be the answer, but problems with conductivity, solution control, and severe etching of the specimens limited the effort directed in this area.

Reliability and consistency are two factors that control the acceptance or rejection of any system. Certainly, the unreliability of the finishing systems investigated and/or the need for high temperature diffusion treatment or the exposure to embrittling gases did not present a favorable picture to the investigators.

The foregoing disadvantages of the electroless nickel system and the embrittling effects of some other metal finishing systems made apparent the acceptable characteristics of a coating to protect the titanium substrate. It was recognized, in addition to providing wear resistance, the process must not seriously effect the physical and mechanical properties of the metal.

The available data found in the literature is very limited with respect to wear characteristics and the effect of the process upon the physical and mechanical properties of the base metal. With the application potential of titanium and its mandatory consideration in aerospace and high speed aircraft, this type of information is urgently needed.

A large volume of available data for metal finishing processing of titanium was thoroughly explored and the duplication of the coating systems attempted. No measurable degree of success resulted from this work.

(C) Conversion Coatings

The next avenue of approach to the problem was conversion coatings, either electrolytic or chemical. The literature revealed several promising possibilities^{10,11}, but upon investigation, these coatings would not satisfy the requirements. The MacMillian Wear Test Machine was employed to determine the wear resistance of these coatings. However, prior to this test, the coatings were evaluated by exposing processed panels to the bristles of a wire wheel traveling at 1750 RPM. Comparison was made to other coatings such as hardcoated aluminum, anodized aluminum, phosphated and black oxide steel samples. With the exception of the hardcoated aluminum, all the coatings tested were not sufficiently dense to withstand the brushing action.

The role of the electrolyte is extremely important in this type of systems investigation. It is known that the electrolyte has sufficient solubility for the product film to produce a dense adherent oxide coating in the hard anodizing of aluminum. In order to produce a coating of any depth the electrolyte should be capable of dissolving the film formed. The rate of film formation is a function of porosity which, in turn, is a function of concentration. The very strong acids such as HF dissolves the coating at too rapid a rate and the remainder is a weak nonadherent coating. It was also determined that anodic coatings of limited depth ($<1000 \text{ \AA}$) could be formed with almost any electrolyte whether acid or basic. To satisfy the requirements for a wear resistant coating, depths far in excess of this amount had to be produced.

APPROACH TO THE PROBLEM

(A) Preparation for Processing

The processing of titanium is considerably simpler than processing required for aluminum and magnesium. All items should be free of burrs, metallic debris, etc., prior to cleaning in a vapor degreaser. Heavy scale and oxides should be removed by acid pickling. The conventional 15-20% HNO_3 and 1% HF by weight solution and operated at a temperature of about 100°F is recommended. After a water rinse the piece should be vapor-honed with #140 grit (40% by volume) water slurry at 80-90 p.s.i. pressure. Normally, machined components are only vapor-honed prior to processing. It has been determined if the natural oxide remains, or, if the vapor honing is not used, then the conversion process will not go to completion, and the resultant coating will be the interference type with a color contingent on the applied voltage.

A positive inexpensive method of protecting areas that do not require the coating has been and still is a problem in anodizing system of high voltages and currents. The laboratory staff at this Arsenal has continually maintained the view that it is more feasible and economical to process an entire component than to use stop-off materials and fixtures. As in the case of aluminum hardcoat, it has been shown that stop-off paints and tapes tend to lift, exposing bare surfaces that may be subjected to a high current surge and subsequent burning and component destruction. However, due to lower voltages in the titanium process, this problem does not approach the severity that is prevalent with aluminum hardcoating, but some pitting may occur in these areas. To further substantiate the omission of stopoff materials in this system, the lack of buildup or coating growth does not change the dimensional characteristics of the processed item. With this distinct advantage the design engineer and processor need not fear interference fits, dimension, or change of pitch on threads; over-size holes, or loose fitting couplings.

The part to be coated is securely fastened to a rack and subsequently to the bus bar in a manner so as to avoid contact with other components, the side walls of the tank, and/or the lead cathode. As in all anodic treatments, the positive line is connected to the component and the

negative line to the lead cathode. The contact points on the component will not be coated during processing. It is possible to reprocess the component to coat these areas.

(B) Materials and Equipment

Materials and equipment described in this section are not necessarily those used in the prototype facility at Watervliet but those which would be required in a production unit.

Processing Tank

Some degree of latitude can be exercised in the selection of a processing tank. The basic requirement calls for a sufficiently reinforced, caustic resistant tank, fitted with outlets for recirculating through a heat exchanger. The tank would have an upper reinforced rim, supporting girths, and flanged outlets at the bottom of the tank; one outlet to be connected to the circulating system and through the heat exchanger, the other to be used for tank drainage. The caustic resistant lining should be brought up over the rim. The tank should be thermally insulated with a 3/4-inch open-celled insulating material bonded to the outside wall, covered with 16-gauge sheet steel, and with a suitable bracket for mounting an external 3/4 hp mixer. Copper bus bars, one inch in diameter and capable of carrying 500 amperes, would be connected in parallel. Two lead cathodes of sufficient area to provide a minimum 1 to 1 cathode-anode ratio should be suspended along the length of the tank. Auxiliary steel cathodes should be connected in parallel with the lead. It would be advisable to support the cathodes in a manner that would prevent any movement due to solution agitation. If additional solution agitation is required, air agitation should be used. An exhaust system with sufficient capacity to remove the fumes liberated should be an integral part of the tank.

It is possible, and in some cases it might be more practical to use a lead-lined tank with auxiliary steel cathodes. In one of Watervliet's prototype units the internal surface of a steel tank was plated. A lead fluoborate solution sufficiently buffered with boric acid and an excess of fluoboric acid was used. Care was taken to deposit the lead into the corners by the use of auxiliary anodes. A total of 1/2-inch of lead was deposited on all sides and the bottom of the tank.

Mixer

Rating of 3/4 H.P., 1750 rpm motor speed; 400 rpm propeller speed, 440 volt, 3-phase, 60 cycles is recommended. It must be cautioned that the anodizing solution is sufficiently heavy to warrant a heavy-duty mixer.

Refrigeration Unit

The capacity of the refrigeration unit can only be determined after the tank capacity has been established. The temperature limitations are modest. A low point of 50°F \pm 10°F would be more than adequate. The

heat input can be established as 50 KW maximum.

In addition to the refrigeration unit, a graphite heat exchanger and a caustic resistant circulating pump would be required. The pump should be large enough to provide an adequate solution circulation for satisfactory heat transfer and tank circulation.

Rectifier

A silicon induction regulated rectifier is recommended with no more than a 5 percent ripple, input of 440V, 3-phase, 60 cycle. The maximum output should be 500 amperes and 100 volts.

Rinse Tank

Tank dimensions are to be governed by the requirements. The tank should be equipped with an overflow-trough for continuous water circulation. A spray-rinse unit would be completely acceptable.

Racks

The racks used in this process are identical with the type and construction used in aluminum hardcoating. Typical racks are shown in Figure 1. The spline is made of aluminum 6061-T6 and the holding grip portion made of titanium. The holding block is drilled and tapped to accommodate the titanium screws. The entire assembly is coated with an acid-caustic plastisol and the screws are bared to allow for movement. Conventional commercial multipronged titanium splines can be used for small components.

(C) Procedure

A large variety of electrolytes were evaluated. Each one was tested with several different cathodes; a current density range up to 300 amps per square foot and at temperatures ranging from 20° to 200°F. The data covering these evaluations are listed in Figure 2. The anodizing system, which provided a coating satisfying the specified requirements, uses an aqueous bath composed of a fixed amount of sodium hydroxide, sodium silicate, titanium dioxide, and activated carbon. The piece to be processed is made anodic and the current raised to the calculated amperage. The voltage is steadily increased to maintain this amperage to overcome the resistance resulting from the formation of the anodic coating. The system is stabilized at about 40 volts and the current slowly decays as the coating continues to form. When a minimum current is reached, the article is removed from the solution. The solution is continuously agitated to maintain the processing bath at a temperature range of 60° to 68° F.

The processing solution to provide the above-mentioned anodic coating is composed of:

	<u>Grams/liter</u>	<u>oz/gal</u>
Sodium Hydroxide (NaOH)	214.5	28.5
Sodium Silicate (Na ₂ SO ₃)	18.75	2.5
Activated Carbon (C)	3.75	.5
Titanium Dioxide (Ti ₂ O ₃)	15.0	2.0
Water to make	1 liter	1 gal.

Anodizing Parameters

Temperature 60° - 68°F

Baume 19.4 (adjust with NaOH)

pH 13.5 - 14

Current Density 36-46 asf (.25 - .3 asi)

In the system pure lead is used as the prime cathode. An auxiliary cathode of low carbon steel with a ratio of 10 lead to 1 steel is connected in series. These cathodes may be individually suspended or the tank lining can be lead with the steel anodes suspended separately. When long tubular sections are processed, an internal cathode is recommended.

Agitation of the bath is necessary to dissipate the heat generated during the process. In the case of any anodic process, the agitation must be sufficient to insure a maximum of 68°F at the solution-metal interface. The coatings formed at temperatures in excess of 68°F are soft and have little wear resistance. The color of this coating will be determined by the applied voltage and the alloy. These are termed interference coatings and have little depth. Then too, the agitation is required to retain the homogeneity of the solution. Without such action the active ingredients will settle out and remain ineffective. This agitation may be accomplished by mechanical means, air circulation, or pumping. In some cases where blind holes are deep or a long cylinder is to be internally coated, auxiliary pumping through or into these areas may be necessary.

In relation to temperature, it has been determined that a maximum of 68°F is necessary to retain the hardness of the coating. A minimum of 60°F has been established but no adverse nor advantageous effects have been noted at temperatures below this point. To maintain the required temperature some means such as cold water cooling coils or the use of a heat exchanger is necessary. The type of cooling system employed could

very well be determined by the volume of solution and the work load to be processed.

A pH of the solution must be maintained at a high level to insure maximum conductivity and hardness, and to assure the solubility of the sodium silicate. The pH of the bath is maintained between 13.5 to 14.0 by the addition of sodium hydroxide. A baume of 19.4° is maintained during processing and is also controlled with sodium hydroxide.

The current density range of the system has been determined to be 35-45 amps per square foot (a.s.f.). The maximum voltage attained at this current density is 40 volts providing the solution is operated within specified parameters. The starting voltage, also referred to as the polarization voltage, is 28 volts. When the starting voltage is reached, the amperage increases from zero to the determined current. The current remains stable for a short period of time, approximately 30 seconds, then slowly decreases. At the minimum current value the current density is about 10 a.s.f. The decrease in current indicates the formation of the coating and the process is complete when the current is stabilized at its minimum value. The entire cycle is complete in about 15 minutes.

Control of the titanium dioxide and carbon content can be determined by chemical analysis. Daily additions of one percent of the basic requirements, 0.45 grams carbon and 2.0 grams titanium dioxide per gallon, per 8 hours of processing are standard.

It is possible to reprocess components without stripping the entire piece. The coating is not an insulator. The original contact points can be covered by repositioning the holding fixture and reprocessing.

RESULTS

The following tables illustrate the results of tests performed at Watervliet Arsenal and other government agencies.

TABLE I

TENSILE TEST

Annealed Ti 6AL 4V		- Ambient Temperature				
SPECIMEN						
Condition	Symbol	Diam. (in.)	Yield Strength (psi)	Tensile Strength (psi)	Elongation (%)	Reduction in Area (%)
Coated	1	.505	127,350	139,750	16.0	45.5
	2	.505	127,950	140,000	16.5	48.6
	3	.503	128,335	140,160	16.5	48.2
	4	.505	127,050	139,250	17.0	50.3
	5	.503	128,030	140,665	16.5	51.0
	R	.505	127,390	140,875	17.0	50.0
Uncoated	c	.505	129,000	139,875	17.5	50.6
	E	.505	127,050	140,875	17.5	49.8
	K	.503	126,975	140,210	17.0	49.4

Test performed at Benet Research and Engineering Laboratory,
Watervliet Arsenal

TABLE Ia

TENSILE TEST

Ti 6AL -4V		Mill Annealed .032"		
Condition	Temp.	Yield Strength F _{tu} (psi)	Tensile Strength F _{ty} (psi)	Elong. (% in 2')
Uncoated	RT	122,500	122,500	10.5
Coated	RT			
Uncoated	550°F	88,100	79,600	12.5
Coated	550°F	90,100	80,500	11.5
Uncoated	700°F			
Coated	700°F	85,200	77,700	14.0
Uncoated	800°F	81,600	67,700	13.0
Coated	800°F	82,200	68,100	13.0

Coated specimens were vapor honed and anodized.
 Uncoated specimens were just degreased.
 Two tests per condition.

Test performed at Air Force Materials Laboratory,
 Wright-Patterson Air Force Base

TABLE Ib

TENSILE TEST - AMBIENT TEMPERATURE

C.P. Titanium - Mill Annealed .034"

<u>Condition</u>	<u>Yield Strength psi</u>	<u>Tensile Strength psi</u>	<u>Elong. %</u>
Uncoated	73,300	89,700	10.5
Uncoated	73,400	88,300	12.7
Coated	72,300	90,500	9.7
Coated	73,100	91,300	9.6
Coated	71,600	87,900	10.6
Coated	70,100	82,900	12.8
Coated	75,200	93,400	16.8

(a) Coated specimens were vapor honed and anodized.

(b) Bar specimens were vapor blasted

Test performed at Benet R&E Laboratories,
Watervliet Arsenal, Watervliet, New York

TABLE II

FATIGUE TEST - ROTATING BEAM

Ti 6AL 4V - Ambient Temperature

<u>CONDITION OF SPECIMEN</u>	<u>CALCULATED STRESS (psi)</u>	<u>CYCLES TO FAILURE</u>
Uncoated	99,000	38,000
Uncoated	61,500	1,075,000 (No failure)
Uncoated	84,000	108,500
Uncoated	84,000	66,000
Coated (2 min)*	84,000	127,000
Coated (3 min)*	84,000	3,765,000 (No failure)
Coated (4 min)*	84,000	1,266,000
Coated (5 min)*	84,000	89,000

Test performed at Benet Research and Engineering Laboratories,
Watervliet Arsenal

* Pertains to time after amperage had reached a minimum level of
.05 amps per square inch.

TABLE III

WEAR TEST

Modified MacMillan Wear Tester
Load: 40,000 psi

SURFACE FINISH		Revolutions to failure
Timken Race	Bearing Block	
Lubricated Hard Coat ²	Lubricated Hard Coat ¹	500,000 **
Lubricated Hard Coat	Lubricated Hard Coat	174,684 **
Lubricated Hard Coat	Lubricated Hard Coat	104,039 **
Lubricated Hard Coat	Bare Steel	51,471
Unlubricated Hard Coat	Unlubricated Hard Coat	43,200
Lubricated Hard Coat	Bare Titanium	37,726
Diffused Electro-less Nickel ²	Diffused Electro-less Nickel ²	31,104 *
Diffused Electro-less Nickel	Bare Steel	25,560 *
Bare Steel	Bare Steel	9,792 *
Diffused Electro-less Nickel (Oxide Removed)	Diffused Electro-less Nickel (Oxide Removed)	9,360 *
Unlubricated Hard Coat	Bare Steel	1,588
Unlubricated Hard Coat	Bare Titanium	593
Electro-less Nickel (No Diffusion)	Electro-less Nickel (No Diffusion)	360
Untreated Titanium	Untreated Titanium	216
Untreated Titanium	Untreated Steel	216

* Watertown Arsenal Data

** No failure occurred

1 Lubricant: Inorganic solids in a thermo-setting resin.

2 Diffused in Vacuum at 1550°F

Test performed at Benet Research and Engineering Laboratories,
Watervliet Arsenal

TABLE IV
APPLICATION TO WEAPONS COMPONENTS

<u>RESULTS OF FIRING</u>				
<u>Weapon</u>	<u>Component</u>	<u>No. of Rounds Fired</u>	<u>Failed</u>	<u>Remarks</u>
90mm, M67	Nozzle	20	No	Part of coating eroded
	Nozzle	400		
107mm, XM130 Mortar Mount	Elevating- screw & nut	1800	No	
81mm, XM129 Mortar Mount	Traverse Shaft	400	No	
	3 link- parts	400	No	
60mm Experimental Dual Purpose Weapon	Tube & Breech	84	No	Coating in bore intact

DISCUSSION OF RESULTS

Acid Electrolytes

Favorable results came from dicarboxy acids and salts of these acids although they were not actually acceptable for wear coatings. Acids such as oxalic, formic, and lactic will form an anodic film and additions of borates will improve the coating hardness. Strong oxidizing acids, peroxides, and weak bases gave results that were not any closer to our requirements. As mentioned earlier, the dicarboxy acids, specifically citric acid and salts of this acid, gave the best results of these series. All through this phase of the study only interference films resulted. Colors ranged from pale yellow through the gold-greens to several degrees of blues.

The literature ^{12,13,14} discusses the formation of interference coatings at low voltages and states that these coatings are less than the .002 inch coating thickness that would meet our requirements for a protective film.

Most of these coatings were formed at voltages under 40 volts but some required up to 200 volts. During the latter phase of the work, it was found that by introducing silicates to a citric acid bath, a barrier layer, grey-gold, was formed with considerably more hardness and depth. Some degree of precipitated titanium dioxide was found on the panel. Despite the formation of interference and barrier layers during the evaluation of these electrolytes, a coating with sufficient durability to be used as a wear resistant coating was not produced.

Alkaline Electrolytes

The emphasis was next directed toward the evaluation of alkaline electrolytes. Work done by Miller, Jeffreys, and Pray at Battelle Memorial Institute indicated promising results with solutions other than acidic systems¹⁵.

The anodizing system developed during this investigation and outlined under "Procedure" satisfied the Arsenal's need for a coating that: (1) would reduce the galling and seizing of titanium, (2) could be applied with comparative ease, (3) would require conventional materials and equipment, and (4) would not adversely effect the base metal. The coating, when comparatively tested with other anodized or conversion coatings for titanium, was considerably more acceptable.

A dual coating is formed by the action of this processing solution. The outer layer is a white, soft precipitate coating of either an oxide or hydroxide of titanium. This coating is easily removed by brushing with a firm bristle brush. The under layer or the coating formed directly on the metal is a barrier layer type coating identified as iron titanate with a probable structure of either $\text{Fe}_2 \text{Ti}_4 \text{O}$ or $\text{Fe}_3 \text{Ti}_3 \text{O}$.¹⁶

The evaluation of the Watervliet coating and the degree of protection afforded has indicated a greater degree of conversion of the base metal than could be expected from a study of the literature covering the investigations of coatings for titanium. As reported previously, films in the area of 5000 to 6000 Å were considered adequate. However, with the developed process conversion to a depth of .004 inches has been verified by microphotography. It is apparent that this depth of conversion would affect the degree of protection and the mechanical and physical properties considerably more than the thinner oxide coatings. This can be considered analogous to the conversion of aluminum to a hard and soft anodic coating. The soft anodic coatings have little, if any, effect on the fatigue strength. The hard coat for aluminum, however, decreases the fatigue strength by as much as 40 percent¹⁷.

It has been demonstrated in laboratory tests and in operational application that the coating does not adversely affect the titanium metal. As noted in Tables I, I(a), and I(b), the tensile properties of the Ti 6AL-4V have not been altered by the treatment. Microscopic examination of the fractured surfaces showed that the coating was relatively ductile and adherent to the base metal. No chipping or cracking was noted along the entire specimen length. The absence of brittle fracture or the retention of ductility noted in all these tests strongly indicates a lack of embrittling effect from the process.

The study relating to the effects of the process on fatigue life has shown encouraging results. The rotating beam test (Table II) indicates no deleterious effects but rather a marked increase in life upward to 30 times that of an uncoated specimen. These specimens were coated under carefully controlled conditions and comparable results would be difficult to obtain consistently in a production type operation.

It is held by various authors that fatigue cracks result from pre-existing microcracks, or they are nucleated at stress concentrations such as notches, inclusions, or other inhomogeneities in a material. It is shown in Figures III and IV that the coating is quite homogeneous and free of inclusions. It also smooths the original surface being remarkably free of either cracks or steps. This homogeneity could be an explanation for the extended fatigue life.

The data in Table III represents work performed at Watervliet and Watertown Arsenal.¹⁸ In this series of tests the resistance of the coating to wear is clearly indicated. Equally important is the ability of the coating to accept a dry film lubricant and to retain the film over an extended wear period. The lubricated specimen, tested through 500,000 revolutions, was periodically retested for an additional 200,000 revolutions with no signs of failure. Consistent with the acceptable performance of the dry film lubes, a hydraulic actuator tested with liquid lubrication proved satisfactory in a 225-hour functional test.¹⁹ A critical evaluation of the results points out the importance of mating coated titanium against coated titanium or of providing some means of lubrication in addition to the anodized coating.

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h.
The list of actual weapons components found in Table IV reflects the range of possible application to cannon and mortar assemblies. The firing test of the 90mm M67 recoilless rifle nozzle showed a high degree of protection for the titanium substrate. An uncoated breech showed areas of metal removal after a few rounds, but the coated nozzle showed no erosion after 20 rounds and metal removal did not occur until 400 rounds were fired. Figure V shows two of the breech nozzles that were fired during this test. The specimen on the right was electroless nickel-coated and failed under 10 rounds. The nozzle to the left failed after 400 rounds.

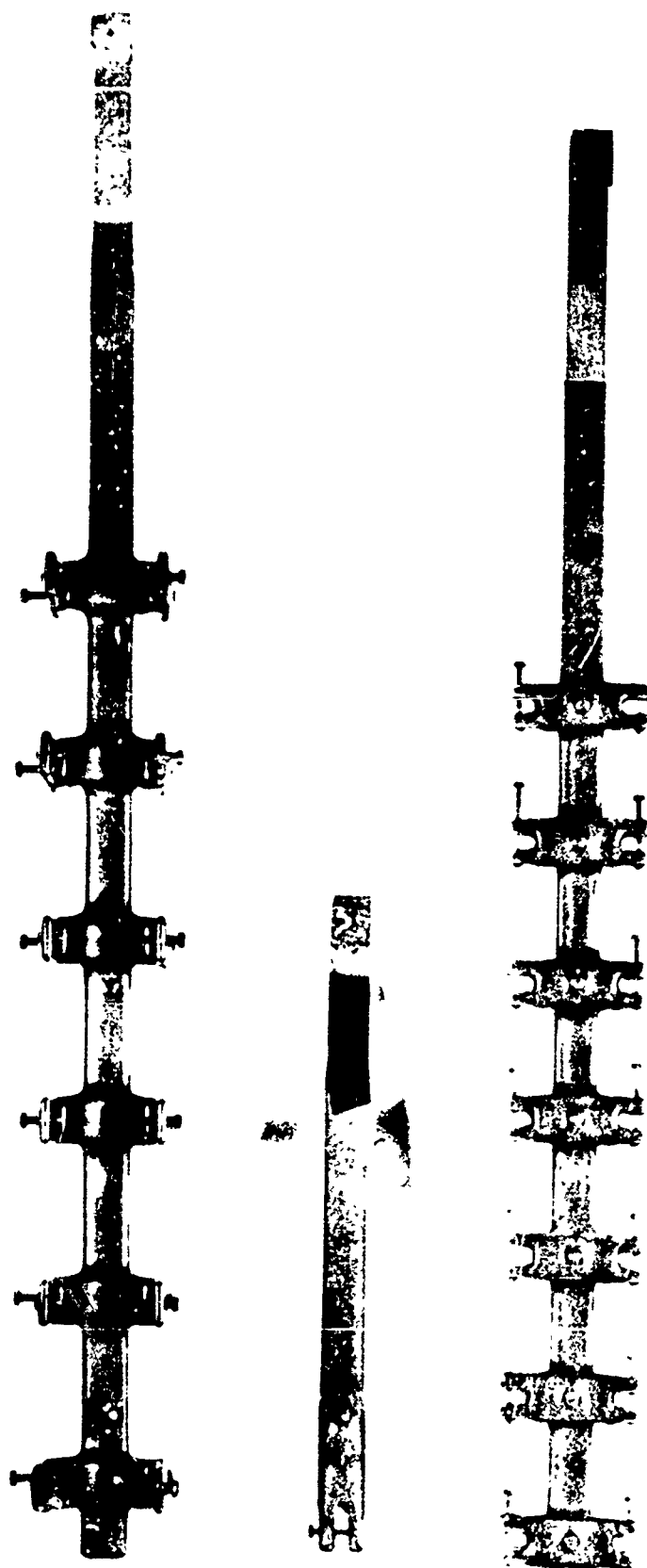
The components of the 81mm and 107mm mortars were subjected to vigorous testing under field conditions. No malfunction of the coated parts occurred during this phase of testing. No lubrication was used with either of these two weapons. Figure VI illustrates typical coated titanium mortar components.

The wear and impact resistance of the coating is demonstrated in the test of the 60mm weapon. The 84 rounds fired did not adversely affect the tube or breech. Dimensional readings and visual observation did not show evidence of wear or galling after this firing sequence. Additional firing tests will be conducted in the future to determine the effective life of the titanium components and the coating.

CONCLUSIONS

A review of the results points out rather conclusively that:

1. While the anodized coating assists in many areas, it does not adversely affect the mechanical and physical properties of titanium.
2. The main objective of the program was realized with a marked increase in the resistance of titanium to alling and seizing.
3. The wear tests clearly demonstrate the need for some lubrication or the need for mating anodized components.
4. The coating does not possess the wear characteristics of hard-coated aluminum, but at its lowest rating, it will provide more protection than many other coatings tested in the laboratory.
5. An evaluation of all potential anodizing solutions cited in the source literature and additional anodizing systems obtained through personal contacts compared with Watervliet Arsenal's process indicates none of these coatings were competitive as far as wear resistance is concerned.
6. The system is typically anodic and requires no sophisticated equipment or controls with respect to the ease of application and control.
7. The voltage and temperature requirements are moderate and the solution can be compounded from inexpensive and easily obtainable chemicals.



Acid Electrolytes - 1 Liter Volume			Temp.	Min.	Max.	Cath-	Time	Remarks
			°F	Amp.	Volts	ode	in Min.	
Chromic Acid 250g + water			26-180	.5	20	Pb,Fe Pt	15-30	Soft Coatings
Chromic Acid 250g + Oxalic Acid 25g + water			26-180	1.1	10	Pb,Fe	15-30	Soft Coatings
Chromic Acid 250g + water			0-25	1.5	5	Pb	30	Soft Coating
Nitric Acid 10ml - 90ml + water			35-110	.5	35	Pb	15-30	Soft Coating Pitting
Sulfamic Acid 10ml - 90ml + water			35-180		35	Pb	15-30	Soft Coating Pitting
Lactic Acid 10ml - 90ml + water			35-150	1	20	Pb,Fe	15-30	Soft Coating
Maleic Acid (30ml - 50ml) + water			50-110	1	20	Pb,Fe	15-30	Soft Coating
Citric Acid 200g + water			80	1	40	Steel	15	Fair Hardness *
Citric Acid 200g + water			30	2	40	Steel	15	Fair Hardness *
Citric Acid 200g + water			28	2	40	Pb	10	Not as hard *
Citric Acid 200g + water			30	.05	.05	Pb	20	Fair Hardness *
Citric Acid 200g + water			28	.10	40	Pb	20	Fair Hardness *
Citric Acid 100g + water			-30	1	40	Pb	15	Green-gold coating. Fairly hard
Citric Acid 100g + Sulfamic Acid 22g + water			28	2	45	Pb	15	Silver-Green Coating. Fairly hard.

* Could not get sufficient Amperage - Maximum Amp -4

Figure 2. Electrolytic Solutions Utilized

Figure 2 (Continued)

Acid Electrolytes - 1 Liter Volume	Temp. °F	Min. Amp.	Max. Volts	Cath- ode	Time in Min.		Remarks
Citric Acid 100g + Sulfamic Acid 22g + water	36	2	45	Pb	22		Soft Coating
Citric Acid 100g + Sulfamic Acid 22g + water	27		35	Pb	10		No Current Flow Soft Coat
Citric Acid 50g + Oxalic Acid 25g + water	30	.01	45	Pb	20		Soft
Citric Acid 150g + Oxalic Acid 25g + Water	27	.5	35	Pb	20		Soft
Citric Acid 150g + Oxalic Acid 50g + water	20-40	.1	35-40	Pb	20-30		Soft
Citric Acid 300g + Hydrogen Peroxide 50g + water	24	.1	40	Pb	50		Silver-grey Soft
Citric Acid 506g + Hydrogen Peroxide 25g + water + Acetanilide 10g + water	140	1	35	Pb	5		Enter with curr- ent on - Voltage 35 - Conversion Started - Controls Malfunction
Sulfuric Acid (66°) 85ml + Oxalic Acid 7.5g + water	14	.1	20	Pb	15		Gold Coating Semi-hard
Sulfuric Acid (66°) 85ml + Oxalic Acid 7.5g + water	14	.15	30-70	Pb	30		Coating Softened as voltage went up.
Phosphoric Acid 65g + Sodium Hypophosphite 20g + Hydrogen Peroxide (20%) 50g + water	130-170	2-4	20-70	Pb	30		Poor in all runs.
Hydrofluoric Acid 20ml + Oxalic Acid 380ml	86	.1	20	Pb	30		Did not anodize
Hydrofluoric Acid 20ml + Oxalic Acid 380ml	86	.5	20	Steel	30		Soft - Spotty
Formic Acid 100g + water	34-42	.5	35	Pb	15		Soft - Yellow

Figure 2 (Continued)

Figure 2 (Continued)

Acid Electrolytes - 1 Liter Volume	Temp. of	Min. Amp.	Max. Volts	Cath- ode	Time in Min.	Remarks
Gluconic Acid 20ml + Citric Acid 400g + water	100	1	35	Pt.	20	Soft Coating
Oxalic Acid 90g	80	.01	5	Pb	60	Purple Coat
Oxalic Acid 90g	210	1	5		30	Soft Blue
Oxalic Acid 100g - Ethyl Alcohol 500ml	25	1	25	Pb	30	Some hardness
Oxalic Acid 100g - Ethyl Alcohol 500ml	8	.25	35	Pb	15	Indigo
Oxalic Acid 90g - Hydrogen Peroxide (30%) -10ml	30	.25	35	Pb	30	NG
Oxalic Acid 50g + Sodium metaborate 25g + Sodium Chloride 25g + H ₂ O	25	1.5	20	Pb	30	Severe Pitting
Oxalic Acid 40g + Potassium Sodium Tartrate 40g + water	30	.7	20	Pb		Yellow Soft Coat- ing.
Oxalic Acid 40g + Potassium Sodium Tartrate 40g + water	40	.5	35	Pb	30	Blue - soft.
Oxalic Acid 40g + Potassium Sodium Tartrate 40g + Et Alcohol 250ml + water	15-40	1	35	Ti	60	Blue - soft.
Fluoboric Acid 50% b/v - Sodium Metaborate 20g	77	.05	35	Pb	15 Sec.	Blue - Gray - Soft
Fluoboric Acid 50% b/v - Sodium Metaborate 20g	78	.25	35	Pb	30	Blue - Gray - Soft
Fluoboric Acid 50% b/v - Sodium Metaborate 20g	40	.05	35	Pb	35	Slight Improve- ment.
Fluoboric Acid 50% b/v - Sodium Metaborate 20g	40	.05	36	Pb	60	Slow increase in voltage - Sl. Harder

Figure 2 (Continued.)

Acid Electrolytes - 1 Liter Volume	Temp. °F	Min. Amp.	Max Volts	Cath- ode	Time		Remarks
					In	Min.	
Fluoboric Acid 50% b/v - Sodium Metaborate 20g	22	.03	150	Pb-Pt	60		Soft Coating
Fluoboric Acid (48%)	77	.05	35	Pb	15		Blue-Grey-Soft
Boric Acid 120g - Water	30	.05	35	Pb	65		Showed some promise. Hard- ness fair.
Hydrochloric Acid (21%) 25ml + Sodium Sulfite 50g + Sodium Dichromate 50g + water	33	.1	35	Pb	30		Pitting - Soft Coating
Hydrochloric Acid (37%) 50ml. + Oxalic Acid 30g + Nitric Acid (28%) 10ml + water	10	.2	70	Pt	15		Soft Coating

Electrolyte - 1 Liter Volume	Temp. of	Min. Amps.	Max Volts	Cath- ode	Time in Min.	Remarks
Hydrogen Peroxide 50ml, Benzol Peroxide 60g Ethyl Alcohol 950ml	-50	.05	35	Ti	15	Gold Color - Soft
Hydrogen Peroxide (30%) 6% b/v + water	8-32	.05	36-50	Pb+Pt	30-60	Gold interference Some hardness
Hydrogen Peroxide (30%) 15% b/v	26	.05	36	Pb	30	Gold interference
Hydrogen Peroxide (30%) + 3g Calcium Chloride 6% b/v + water	208	5	36	Pb	60	Soft coating
Hydrogen Peroxide (30%) 50ml + Benzol Peroxide 60g + Ethyl Alcohol 950ml	-50	.05	35	Ti	10 sec	Fair
Hydrogen Peroxide (30%) 50ml + Benzol Peroxide 60g + Ethyl Alcohol 950ml	0	.05	30	Ft	10	Fair
Hydrogen Peroxide (30%) 400g + Acetanilide 10g + water	12	1.5	35	Ti	60	Spotty coating Some areas of hardness.
Hydrogen Peroxide (30%) 400g + Acetanilide 10g + water	28	1	35	Ti	60	No improvement
Hydrogen Peroxide (30%) + Sulfuric Acid 10ml + water	24	.01	35	Pb	30	Coating more dense at lower voltage
Hydrogen Peroxide (30%) + Sulfuric Acid 10ml + water	24	.5	10	Pb	30	More dense but not sufficiently hard
Hydrogen Peroxide (30%) 400g + Sodium Hypophos- phite + Acetanilide 10g + water	30	2	70	Pb	15	Some hardness to coating - Diffi- cult to control temp. - Rise of 64°

Figure 2A. Electrolytic Solutions Utilized

Figure 2A (Continued)

Electrolyte - 1 Liter Volume	Temp. °F	Min. Amps.	Max. Volts	Cath- ode	Time in Min.	Remarks
Hydrogen Peroxide (30%) 400g + Sodium Hypophos- phite 10g + Acetanilide 10g + water	30	.5	35	Pb		Could not control temp.
Hydrogen Peroxide 30% - 700ml + Acetanilide 10g	15-20	.05	50	Pb		Semi-hard coat Poor cooling
Potassium Sodium Tartrate 70g - water	36	.5	35	Pb	30	Soft
Potassium Sodium Tartrate 100g + Hydrogen Peroxide 50g + water	30	.25	75	Pb+Ti	15	Harder than aver- age coating
Thiourea 300g + water	180	.5	35	Pb+Ti	15	Soft
Thiourea 30g + Oxalic Acid 100g + water	130	.5	35	Pb+Ti	15	Soft
Thiourea 200g + Citric Acid 100g + water	180	.25	35	Pt	20	Fairly soft coat- ing
Potassium Sodium Tartrate 200g + Citric Acid 20g + Hydrogen Peroxide 20ml + water	34	2	30	ZN	2	Soft
Potassium Sodium Tartrate 200g + Citric Acid 20g + Hydrogen Peroxide 20ml + water	78	3	30	ZN	2	Much softer
Ethyl Alcohol 500ml + Boric Acid 10g + Sodium Meta Borate 20g	22	.03	7	Pt	60	Purple Soft coat- ing
Ethyl Alcohol 500ml + Boric Acid 10g + Sodium Meta Borate 20g	20	.03	120	Pt	45	Pink-Soft coating
Ethyl Alcohol 500ml + Boric Acid 10g + Sodium Meta Borate 20g	22	1	150	Pt	60	Lt. Blue - No G
Ethyl Alcohol 200ml + Sodium Meta Borate 25g	30	1	70	S.S	30	Slightly harder

Electrolyte - Salts	Min. Amps	Max. Volts	Cathode	Time in Min.	Remarks
Sodium Gluconate 100g + Citric Acid 50g + water	.5	32	Pb, Fe Pt, Ti	30	Blue-Grey Color Soft coat
Sodium Gluconate 200g + Citric Acid 50g + water	.5	35	Pb	30	Blue-Grey Color Soft coat
Sodium Gluconate 200g + Sulfamic Acid 50g + water	1.0	35	Pb	30	Grey-gold - Fair coating
Sodium Gluconate 200g + Sodium Carbonate 25g	.5	36	Pb+Ti	30	Grey - Fair coating
Sodium Gluconate 200g + Sodium Carbonate 50g + water	.25	36	Pb+Ti	15-30	Grey-blue Color Fair coating
Sodium Gluconate 200g + Sodium Hydroxide 50g + water	.5	10	Pb+Pt	15-30	Grey-Green Color Some hardness
Sodium Citrate 100g + Sulfamic Acid 5g + water	1	32	Pb		Green-gold - soft
Sodium Citrate 100g + Sodium Carbonate 50g + water	5	35	Pb+Pt		Green-gold - soft
Sodium Citrate 100g + Sodium Hydroxide 25g + water	.5	35	Pb		Grey-Blue - Fair Hardness
Sodium Citrate 100g + Sodium Hydroxide 25g + Hydrofluoric Acid 2ml + water	5	32	Pb+Ti	15	Spotty - White Soft spots
Sodium Citrate 100g + Sodium Hydroxide 25g + Sodium Fluoride 10g + water	2	38	Pb+Ti	30	More uniform - White top coat Some hardness of Light Grey under- coating

Basic Electrolytes 1 Liter Volume	Temp. °F	Min. Amps	Max. Volts	Cath- ode	Time in		Remarks
					Min.	Max.	
Sodium Hydroxide 100g + water	203	.5	35	Pb	15-30		Coating formed but dissolved due to erratic amperage & temp
Sodium Hydroxide 100g + water	0-36	.5	36	Pb	30		Coating formed but dissolved due to erratic amperage & temp
Sodium Hydroxide 100g + water	40-212	.5	36	Pb	30		Coating formed but dissolved due to erratic amperage & temp
Sodium Silicate 10g + Citric Acid 50g + Hydrogen Peroxide 25g + Acetanilide 10g + water	140		35	Pb	5		Bath Gelled
Sodium Silicate (43° Be') 200ml + Hydrogen Peroxide 25ml	140	2	20	Pb, T1	10		Soft coating Bath unstable
Sodium Silicate (43° Be') 200ml + Sodium Carbonate 50g + water	210	0	35	Pb	10		Some improvement
Sodium Hydroxide 200g + Sodium Silicate (43° Be') 100ml + water	135	1	20	Pb	20		Promising - Harder than other coatings 2 layer coating
Sodium Hydroxide 200g + Sodium Silicate 305g + water 2850g	92	.02	25	Pb	20		Fairly soft Outside coating very soft

Figure 2C. Electrolytic Solutions Utilized

Figure 2C (Continued)

Basic Electrolytes	J. Liter Volume	Temp. of	Min. Amps.	Max. Volts	Cath- ode	Time in		Remarks
						Min.	Max.	
Sodium Hydroxide 200g + Sodium Silicate 305g + water 2850g		90	.02	30	Carbon	15		Fairly hard Carbon anode helped
Sodium Hydroxide 200g + Sodium Silicate 305g + water 2850g + activated carbon		110	0	35	Pb	20		Increased hardness over other NaOH baths.
Sodium Hydroxide 1000g + Sodium Silicate 252g Activated Carbon: 45g + water 14,000ml 29.4°Be'		88	0	35-40	Pb	90		Good Coating - 2 layer. Bath not too stable - some pitting and etching
Sodium Hydroxide 1000g + Sodium Silicate 252g Activated Carbon 45g + water 14,000ml 29.4°Be' + Titanium Dioxide 10g		70	0	35	Pb	30		Good coat Appears hard- est to date
Sodium Hydroxide (76%) 2000g + Sodium Silicate 43°Be' 252g + activated carbon 45g + Titanium Dioxide 20g + water 14,000ml		65-68	0	35	Pb+Fe	15		Excellent Coat- ing - Two layers - stable bath
Nickel Hydroxide 50g + Citric Acid 100g + water		175	5	35	Pb	15		Soft coating
Nickel Oxide 50g + Oxalic Acid 100g + Citric Acid 100g + water		210	2	15	Pb	15		Soft-thin coating

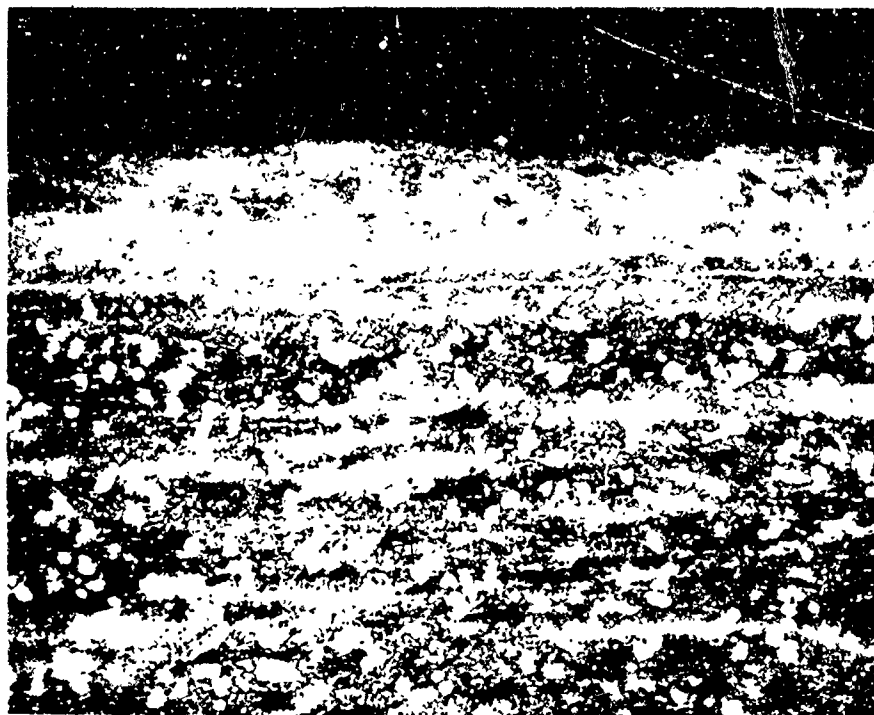


Figure 3. Converted Anodized Film at 250X



Figure 4. Converted Anodized Film at 500X



Figure 5. Erosion Comparison Coated versus Uncoated Titanium Nozzles

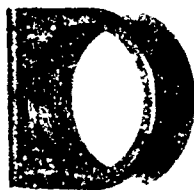
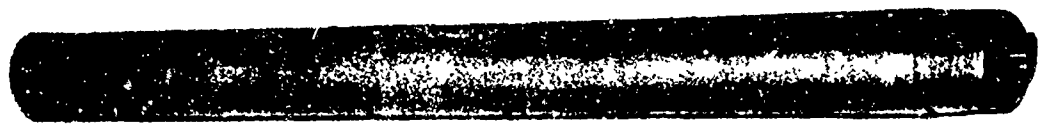


Figure 6. Titanium Coated Components

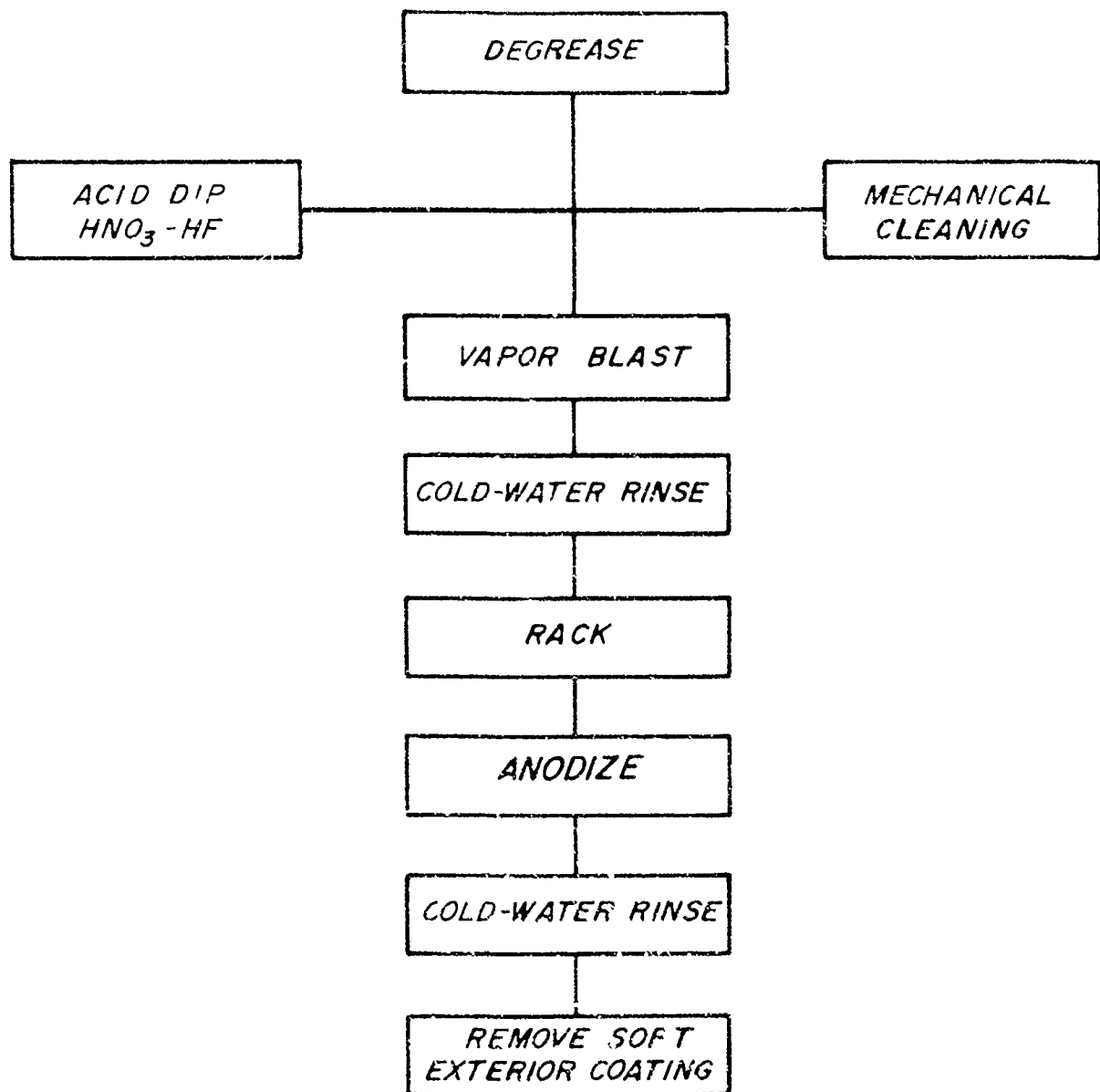


Figure 7. Titanium Anodize Flow Sheet

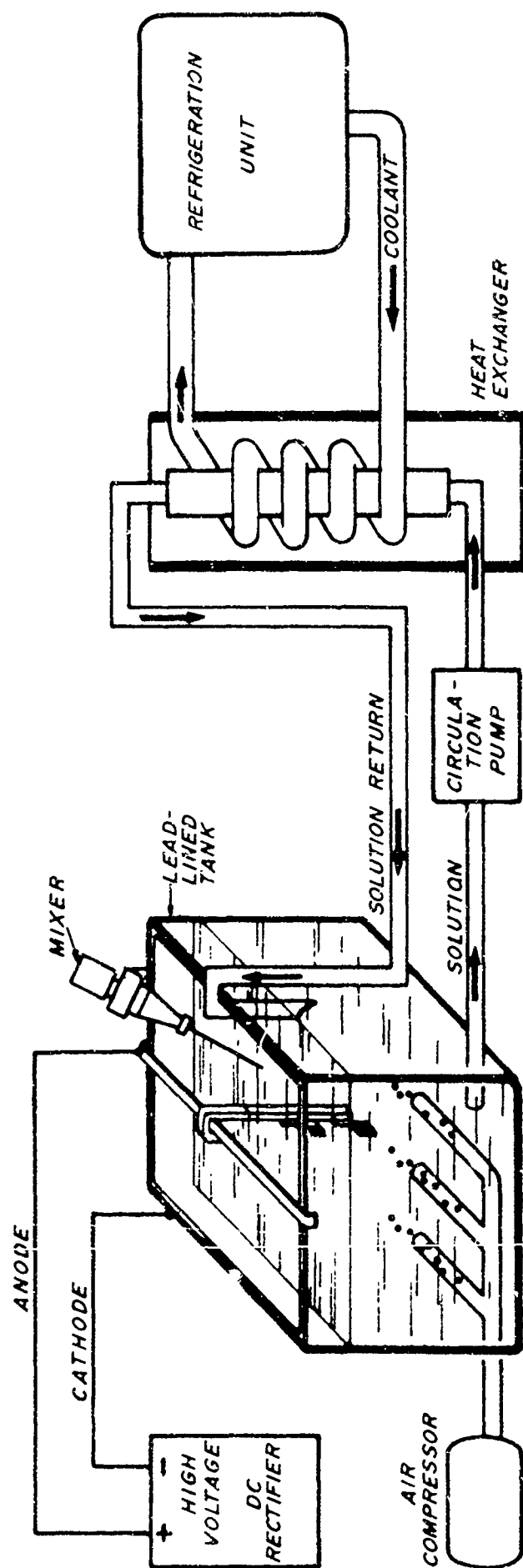


Figure 8. Suggested Layout

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13 ABSTRACT The requirements of an advancing technology in weaponry, aircraft, and aerospace have necessitated a consideration of light metals as a substitute for steel. In the search to reduce weight, and consequently increase mobility, titanium offers valuable assistance. The use of titanium as an engineering and structural material has been accepted for a comparatively short time. This acceptance was predicated on two important factors, strength/weight ratio and corrosion resistance. The tendency of titanium to gall and seize, when used as a bearing or mating surface, has restricted a full utilization of the metal. Work conducted at Watervliet Arsenal to develop a process that reduces or eliminates this condition has been evaluated. Processing details, a summary of test data covering wear resistance, and the effects of the process on the mechanical properties of titanium are discussed.		

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